

## Polymer Communication

## Super-tough poly(lactic acid) materials: Reactive blending with ethylene copolymer

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## ABSTRACT

Poly(lactic acid) (PLA) is well known as a biocompatible, bioresorbable, and biodegradable polymer superior to petrochemical polymers from the standpoint of total energy consumption and life-cycle CO<sub>2</sub> emission, since it can be obtained from natural sources. However, the brittleness of PLA is a big drawback for its wide application. Although many studies have been carried out modifying PLA, there is very limited work on reactive blending of PLA. This study demonstrates a dramatic improvement in the mechanical characteristics of PLA by its reactive blending with poly(ethylene-glycidyl methacrylate) (EGMA). It is shown that the interfacial reaction between the component polymers contributes to the formation of super-tough PLA materials, superior to benchmark acrylonitrile–butadiene–styrene (ABS) resins. The novel material highlights the importance of interface control in the preparation of multi-component materials.

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## 1. Introduction

Many studies have been carried out blending PLA with various polymers including poly(3-hydroxybutyrate) (PHB) [1], poly(methyl methacrylate) (PMMA) [2], poly(vinyl acetate) (PVAc) [3], poly(ethylene oxide) (PEO) [4], poly( $\epsilon$ -caprolactone) (PCL) [5,6], poly(ethylene-co-vinyl alcohol) (EVOH) [7], poly(*p*-dioxanone) [8], poly(vinyl alcohol) (PVA) [9], poly(4-vinylphenol) (PVPh) [10], polyethylene (PE) [11–13], poly(hydroxy ester ether) (PHEE) [14], poly(butylene adipate-co-terephthalate) (PBAT) [15], poly(butylene succinate) (PBS) [16,17], and starch [17–19]. In these PLA blends, some systems are reported to have miscibility or partial miscibility, for example PLA with PMMA, PVAc, PVPh, and PHEE. However, most of the systems are immiscible, so that in order to achieve good properties it is essential to compatibilize the systems. It is known that compatibilization can be achieved by addition of polymers with emulsifying properties such as graft or block copolymers. This is done in two manners. One is by the addition of pre-made copolymers and the other is by an *in situ* reaction between the component polymers during melt-blending that form copolymers at the interface [20–22].

There is very limited work on the modification of PLA by blending carried out using *in situ* reactions. One example is a material composed of PLA blended together with low molecular weight PCL and high molecular weight PCL prepared by melt-blending and using the ester exchange reaction by alcoholysis for the *in situ* reaction [5]. It was observed that the miscibility among the three component polymers was improved greatly as a result of the *in situ* reaction. Another example is PLA melt-blended with EVOH in the presence of an esterification catalyst, which induces a reaction between the hydroxyl groups of the EVOH and the terminal carboxyl group of PLA [7]. It was observed that the biodegradation of the PLA/EVOH blend formed with the reaction took place more slowly than that of a simple PLA/EVOH blend prepared without the catalyst.

Attempts have been also made to react PLA with coupling agents composed of diisocyanates or triisocyanates in blends of PLA/starch [18] and PLA/PBS/starch [17]. The reaction between the hydroxyl groups of these biodegradable polymers and the isocyanate group resulted in copolymers containing urethane linkages.

In this study, attention was focused on the improvement of the mechanical characteristics of PLA by reactive blending of PLA with EGMA. This report focuses on the importance of interface control in the preparation of multi-component materials, in which the interfacial reaction between PLA and EGMA successfully modified brittle PLA to a super-tough material.

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## 2. Experimental

### 2.1. Materials

Two kinds of poly(lactic acid) (PLA) manufactured by Mitsui Chemical Co. Ltd were used in the present study: Lacea (H100), PLA-L with lower molecular weight and Lacea (H400), PLA-H with higher molecular weight. It is reported that they contain ca. 1–2% of D-lactide with the rest being L-lactide. A random copolymer of poly(ethylene-glycidyl methacrylate) (EGMA) containing 30 wt% of methylacrylate and 3 wt% of glycidyl methacrylate was supplied from Sumitomo Chemical Co. Ltd. Characteristics of these component polymers are summarized in Table 1. For comparison, notched impact tests were also performed on a sample of acrylonitrile–butadiene–styrene (ABS) copolymer manufactured by Asahi Kasei Co., Stylac 220, as a representative high impact strength material originated from fossil fuels.

PLA and EGMA were melt-mixed in a twin-screw extruder (Technovel KZW15-30MG with  $L/D = 30$ ,  $D = 15$  mm) at 210 °C with a screw rotation speed of either 30 rpm or 200 rpm. Dumbbell-shaped multipurpose test specimens (ISO 3167) of the resultant blends were prepared by injection molding. Some specimens were further treated by annealing at 90 °C for 2.5 h in a conventional oven.

### 2.2. Characterization

#### 2.2.1. Mechanical tests

Tensile properties were determined using a Tensilon UTM-III-10T (Orientec Co. Ltd.) at a tensile speed of 10 mm/min following the ISO 527 procedure. The flexural modulus was measured according to the ISO 178 procedure at a speed of 2 mm/min. Notched Charpy impact tests were performed in an edge-wise placement using a tester (Toyo Seiki Co. Ltd.) with a pendulum hammer of 4.0 J following the ISO179 procedure at room temperature.

#### 2.2.2. Transmission electron microscopy (TEM)

Samples first cryo-microtomed at –60 °C and then stained by ruthenium tetroxide ( $\text{RuO}_4$ ) vapor were observed by transmission electron microscopy (Hitachi type H7000TEM) with an acceleration voltage of 75 kV.

#### 2.2.3. Thermal analysis and X-ray diffraction

Glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and crystallinity ( $X_c$ ) of specimens were estimated under a nitrogen atmosphere with a differential scanning calorimeter (Perkin Elmer, DSC 7) at a heating rate of 10 °C/min. The heat deflection temperature (HDT) was estimated in a flat-wise placement (Toyo Seiki HDT 3M-2) under a 1.80 MPa load with a heating rate of 2 °C/min. Wide-angle X-ray diffraction (WAXD) patterns (Rigaku Co. Ltd. Ultrax8000) were obtained at a scanning speed of 2°/min.

**Table 1**  
Characteristics of component polymers.

	$M_n^b$ (g/mol)	$M_w^b$ (g/mol)	$T_g^c$ (°C)	$T_m^c$ (°C)	MFR <sup>d</sup> (g/10 min)
PLA-L <sup>a</sup>	85,000	129,000	61.1	161.3	8
PLA-H <sup>a</sup>	130,000	198,000	61.5	167.0	3
EGMA	59,600	198,900	–33.8	66.3	9

<sup>a</sup> Containing ca. 1–2 wt% of D-lactide, the rest being L-lactide.

<sup>b</sup> Measured by GPC using chloroform as eluent.

<sup>c</sup> Measured by DSC at a heating rate of 10 °C/min.

<sup>d</sup> Measured at 190 °C under 2.16 kg load, which is reported by a manufacturer.

## 3. Results and discussion

### 3.1. Morphology of the PLA blends

The PLA/EGMA blends were prepared by melt-mixing two kinds of PLA (PLA-L and PLA-H) and EGMA. TEM micrographs of as-prepared PLA/EGMA blends are shown in Fig. 1, in which  $\text{RuO}_4$  preferentially stains the EGMA dispersed phase, providing a sharp contrast. Fig. 1(a) shows results for a (95/5) PLA-L/EGMA blend (numbers in parenthesis indicate weight proportions) and Fig. 1(b) displays results for an (80/20) PLA-L/EGMA blend prepared at screw rotation speeds of 30 rpm (denoted as L95-30 and L80-30, respectively). The EGMA dispersed phase located in the PLA matrix was respectively 0.2–1  $\mu\text{m}$  and 0.2–2  $\mu\text{m}$  in diameter for these samples. Fig. 1(c) shows results for an (80/20) PLA-L/EGMA blend and Fig. 1(d) for an (80/20) PLA-H/EGMA blend prepared at screw rotation speeds of 200 rpm (denoted as L80-200 and H80-200, respectively). For these samples prepared at higher rotation speeds the EGMA domain sizes were drastically reduced to 100–300 nm and 50–200 nm, respectively.

Here, it is considered that the epoxide group incorporated in EGMA will react with both the carboxyl groups and the hydroxyl groups located at the PLA chain ends during melt-mixing. As a result of the reaction, graft copolymers are formed *in situ* at the interface [11,23].

If the difference in density between EGMA (0.960 g/cm<sup>3</sup>) and PLA (1.260 g/cm<sup>3</sup>) is taken into account, the EGMA phase is estimated to occupy 24.7 vol.% in the (80/20 by weight) PLA/EGMA blends. However, it is shown in Fig. 1(d) that the area fraction of the domains is much higher than the estimated fraction and that there are a lot of domains of 50–100 nm in diameter, corresponding to the size of micelle structures, composed of copolymers [24,25]. A drastic reduction in the interfacial tension by the copolymers and the higher melt viscosity of the PLA-H over that of PLA-L likely create a higher shear force during melt-mixing and facilitate the pull-out of the generated copolymers from the interface to the matrix. The new interface created as a result of the removal of copolymers from the interface would generate more copolymers.

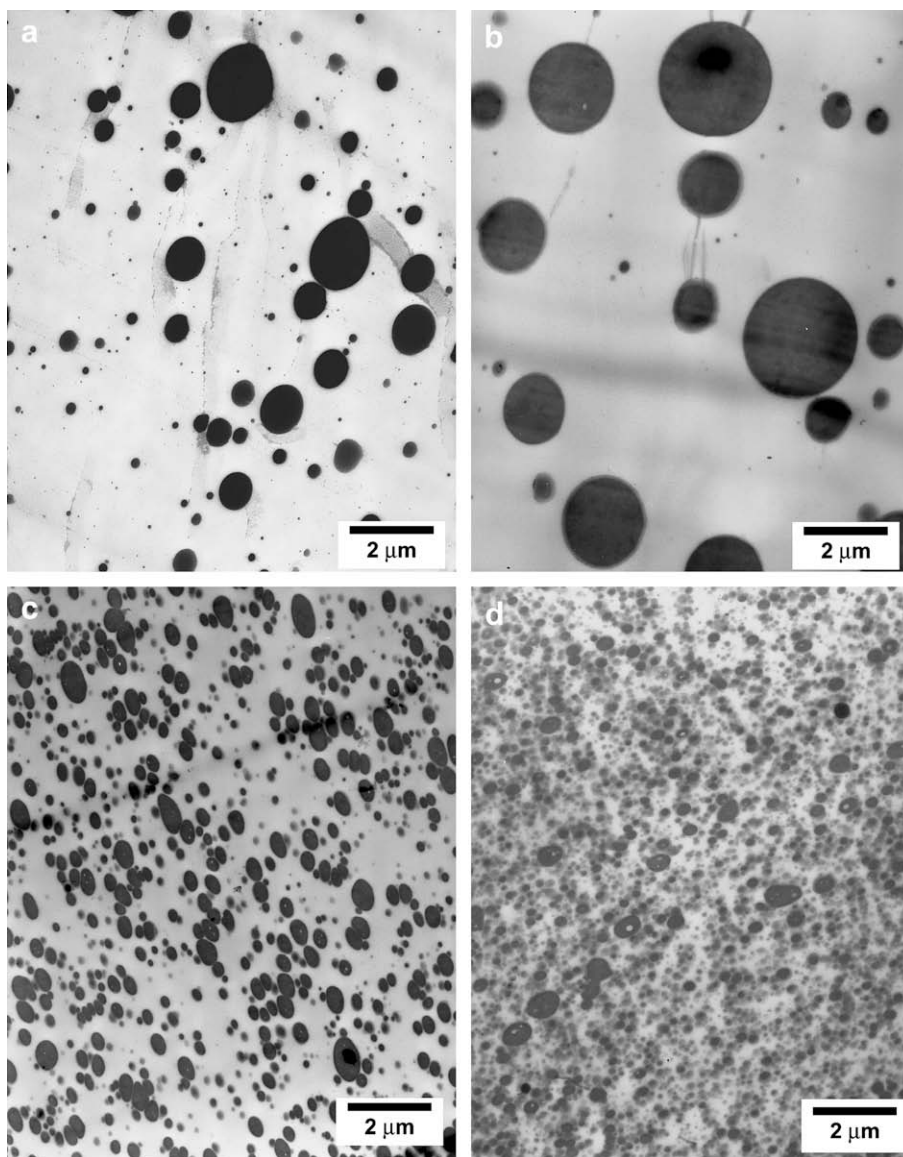
### 3.2. Crystallization

Fig. 2(a) and (b), respectively show heating DSC thermograms of neat PLAs and the PLA/EGMA blends as-prepared and after annealing at 90 °C for 2.5 h. Fig. 2(a) shows two exothermic peaks due to crystallization: cold crystallization ( $T_c$ ) observed at 90–110 °C, and rearrangement crystallization ( $T_r$ ) observed at ca. 150 °C, just before melting of the crystallites. It should be noted that the  $T_c$  peak in H80-200 was located at the lowest temperature compared to the other systems, probably because the small dispersed phase played the role of a nucleating agent and facilitated crystal growth at numerous locations. Based on these DSC data, the crystallinity ( $X_c$ ) of each specimen was estimated from the following equation:

$$X_c(\%) = 100(\Delta H_m - \Delta H_c - \Delta H_r)/\Delta H_f \quad (1)$$

where  $\Delta H_m$ ,  $\Delta H_c$ , and  $\Delta H_r$  are respectively the enthalpies of melting, of cold crystallization, and of rearrangement of polymer chains. Here, the value of  $\Delta H_f$ , the heat of fusion, defined as the melting enthalpy of 100% crystalline poly(lactic acid), was taken to be 93 J/g from the literature [26].

It was found that the respective values of  $X_c$  for as-prepared specimens were 5.3%, 5.8%, 12.0%, and 14.3%, for PLA-L, PLA-H, L80-200, and H80-200. These results indicate that in the as-prepared specimens the presence of the dispersed phase facilitates



**Fig. 1.** TEM micrographs of PLA/EGMA blends stained by RuO<sub>4</sub> vapor [(a) (95/5) PLA-L/EGMA prepared with screw rotation speed of 30 rpm, L95-30, (b) (80/20) PLA-L/EGMA prepared with screw rotation speed of 30 rpm, L80-30, (c) (80/20) PLA-L/EGMA prepared with screw rotation speed of 200 rpm, L80-200, and (d) (80/20) PLA-H/EGMA prepared with screw rotation speed of 200 rpm, H80-200].

crystallization of PLA. Furthermore, after annealing the specimens at 90 °C for 2.5 h, the crystallinity of both neat PLAs and PLA/EGMA blends increased to as high as *ca.* 40%: 45.2%, 34.7%, 41.1%, and 38.1%, for PLA-L, PLA-H, L80-200, and H80-200, respectively.

Fig. 2(c) shows WAXD patterns of as-prepared PLAs and PLA blends. A large and broad halo originating from the amorphous region is observed and only a small and broad peak due to the crystalline region is barely visible at *ca.* 21° in the blends. In contrast, in Fig. 2(d) the WAXD patterns of the annealed PLAs and PLA/EGMA show sharp crystalline peaks of PLA at  $2\theta = 16.5^\circ$  and  $19.0^\circ$  in both systems, consistent with the high crystallinity indicated by the DSC measurements. The strongest peak located at  $16.5^\circ$  is attributed to the (110) and/or (200) planes of the PLA crystallites [27].

### 3.3. Mechanical properties and heat resistance

The mechanical properties and heat resistance of the as-prepared specimens are summarized in Table 2. Both PLA-L and

PLA-H are so brittle they only have 5–10% elongation at break. It is clearly shown that addition of EGMA is very effective for overcoming the brittleness of PLA, resulting in a significant increase in the elongation at break. For this a good distribution of the EGMA component is also essential. This is demonstrated by comparison of the tensile result for L80-30 and that for L80-200, in which both systems contain 20 wt% of EGMA. Here, with the higher screw speed used for L80-200, the elongation at break remarkably increased to over 200%, which is more than 40 times higher than that of neat PLA-L. The domains composed of micelles in H80-200 (50–100 nm size) are probably not able to efficiently absorb the energy of the external force, whereas the domains of EGMA surrounded by *in situ* formed copolymers at the interface in L80-200 (100–300 nm) would be capable of dispersing the energy and, thus, to improve mechanical properties. It was also shown that good distribution of the EGMA dispersed phase resulted in a decrease in the modulus, as observed in the flexural (or tensile) modulus of L80-200 being lower than that of L80-30. Although most of the mechanical properties were similar in both L80-200 and H80-200

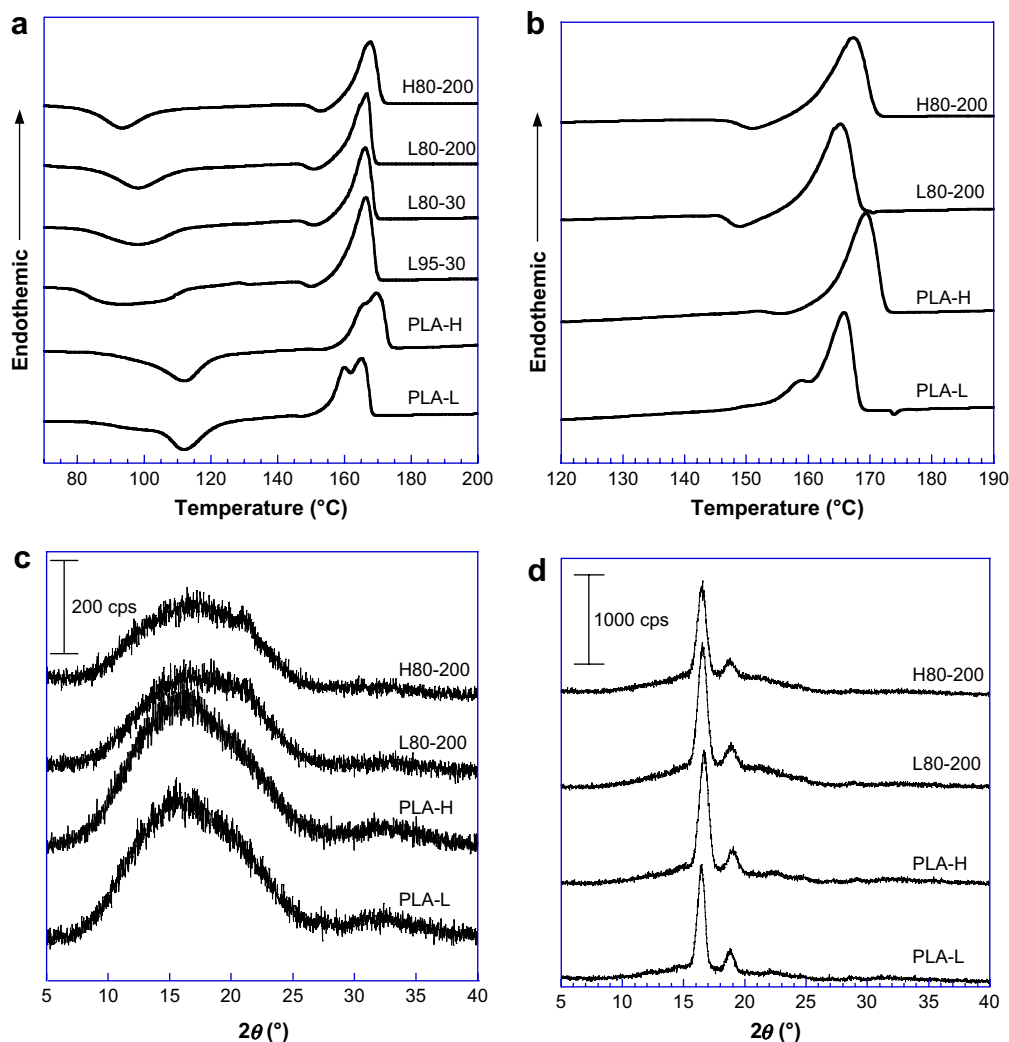


Fig. 2. DSC curves of (a) neat PLAs and PLA/EGMA blends as-prepared and (b) those after annealing, and WAXD patterns of (c) neat PLAs and PLA/EGMA blends as-prepared and (d) those after annealing.

blends, the elongation at break was much higher for L80-200 than that for H80-200.

Similar results for the mechanical properties and heat resistance of annealed specimens are summarized in the same table. Thus, the

**Table 2**  
Mechanical and thermal properties of neat PLAs and PLA/EGMA blends.

	Sample	Tensile tests			Flexural modulus (MPa)	HDT (°C)
		Tensile modulus (MPa)	Yield strength (MPa)	Elongation at break (%)		
As-prepared	PLA-L	1860	64.3	5	2800	55.3
	PLA-H	1890	65.9	11	2750	55.8
	L95-30	–	–	–	–	–
	L80-30	1570	38.1	26	2360	–
	L80-200	1350	40.0	>200	1170	54.2
	H80-200	1310	41.5	89	1190	54.7
Annealed	PLA-L	2560	50.4	3	3950	62.4
	PLA-H	2450	68.8	5	3710	62.7
	L80-200	1600	42.8	12	1920	61.0
	H80-200	1760	44.5	35	1500	60.9

L95-30, L80-30: (95/5) and (80/20) PLA-L/EGMA prepared with screw rotation speed of 30 rpm, and L80-200 and H80-200: (80/20) PLA-L/EGMA and PLA-H/EGMA prepared with screw rotation speed of 200 rpm.

PLA/EGMA samples after annealing showed a higher value than the original as-prepared form in most of the tensile properties such as yield strength and flexural modulus. Although in a previous report the tensile moduli for PLA with 6 and 14% of crystallinity were almost the same [28], the increase of the modulus in the present work is probably associated with a significant increase in crystallinity from 5% to 40%. Annealing increased HDT by *ca.* 7 °C in both neat PLAs and the blends, in which the decrease in HDT by the addition of EGMA was as small as 1–2 °C. These improvements were due to crystallization of PLA. However, the crystallization also caused a drastic decrease in the elongation at break.

Fig. 3 shows the results of notched impact tests. In the as-prepared specimens, the effects of the reactive blending on the impact strength were slight, with the notched impact strength of PLA increased by only a few times. However, surprisingly, after annealing the impact strength of the PLA/EGMA blends increased drastically: the value for the annealed L80-200 was 72 kJ/m<sup>2</sup>, *ca.* 50 times higher than that for the neat as-prepared PLA-L. As-prepared acrylonitrile–butadiene–styrene (ABS) sample measured under the same experimental conditions showed an impact strength as high as 21 kJ/m<sup>2</sup>, however, the present PLA/EGMA far exceeded this strength so that the specimen was unseparable even after hit at high energies of 4 J. It was much beyond expectation that PLA, well



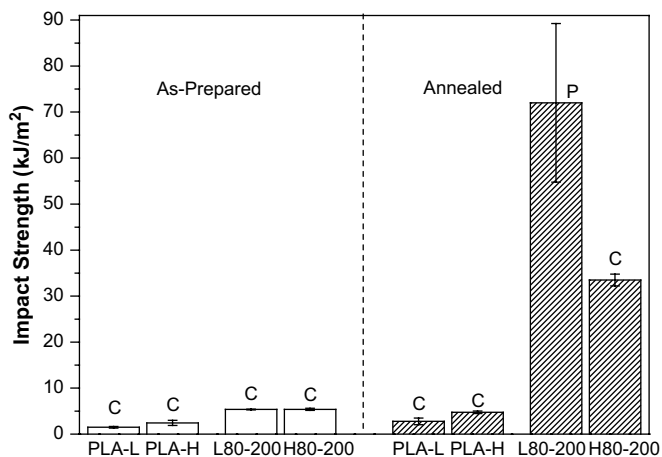


Fig. 3. Notched impact strength of PLAs and PLA/EGMA blends [C: complete break, P: partial break].

known for its brittleness, could be modified to be a tougher material than ABS, without sacrificing other important properties such as heat resistance.

The present results obtained for PLA/EGMA blends are compared to those reported for other PLA blend systems. In one study ternary blends composed of poly(L-lactide) (PLLA), LDPE, and PE-*b*-PLLA prepared by solution blending were studied [12]. The tensile and Izod impact testing results on the ternary blends showed a significant improvement in toughness as compared to the PLLA homopolymer or the corresponding PLLA/LDPE binary blends. For example, in an (80/20/10) PLLA/LDPE/PE-*b*-PLLA sample, which gave the best mechanical properties, the elongation at break and the Izod impact strength increased respectively by 9 times (35%) and by 15 times compared with those of the neat PLA.

In another study the toughening of either semicrystalline PLLA or amorphous PLA was reported, in which PLLA (or amorphous PLA) blends were prepared with LDPE and a PLLA-PE copolymer [13]. Here, two kinds of block copolymers were employed; one with the PLLA block below its entanglement molecular weight, *ca.* 9000 g/mol [29], and the other with the PLLA block above its entanglement molecular weight. It was found that the entanglement between the block copolymer and the matrix at the interface and the crystallization of the matrix significantly contributed to toughening. It was also found that the critical matrix ligament thickness ( $\tau_c$ ), the surface-to-surface dispersed phase interparticle distance, is *ca.* 1.0  $\mu\text{m}$  in these blends.

Here,  $\tau_c$  and entanglement density ( $\nu_e$ ) are recognized as key parameters for rubber toughening in polymer blends [30]. The following relationship between  $\tau_c$  and the characteristic ratio ( $C_\infty$ ) is proposed:

$$\log \tau_c = 0.74 - 0.22C_\infty \quad (2)$$

The value of  $\tau_c$  will change depending on the polymer. For example, polyamide, polypropylene, polyethylene, and poly(ethylene terephthalate) are reported to have values of  $\tau_c$  of 0.3, 0.15, 0.6, and slightly lower than 0.1  $\mu\text{m}$ , respectively [31].

Furthermore, as for the entanglement density ( $\nu_e$ ), it is estimated that  $\nu_e = 0.1 \text{ mmol/cm}^3$  is optimum for toughening, since at this level of entanglement density the occurrence of massive combined crazing and yielding of the matrix is expected [30]. The optimum size of the dispersed phase with 0.1  $\text{mmol/cm}^3$  of  $\nu_e$  is estimated to be *ca.* 0.1–0.3  $\mu\text{m}$  for PLA [32]. This is exactly in the range of size observed in the L80-200 sample shown in Fig. 1(c), so that our results support this prediction. Another reason for the remarkable toughening observed in this study is that the PLA block

of the copolymers formed *in situ* at the interface by reactive blending is trapped in the crystallized structure of the PLA matrix, which results in an increase in interfacial adhesion and hence high impact strength, as reported in a previous study [13].

Lastly it is noteworthy that the well-known brittleness of PLA can be overcome by reactive blending without sacrificing its thermal properties, and that the addition of only a small amount of a reactive copolymer is enough to toughen the PLA. The inherent terminal groups of PLA reacted efficiently with the epoxide groups in the copolymer during melt-mixing, which resulted in super-tough PLA materials. It was also deduced that crystallization of the PLA matrix plays a significant role in the toughening. There are few reports in PLA blends pointing out the effects of crystallization.

#### 4. Conclusion

Very high performance of PLA blends was obtained by reactive blending of PLA and EGMA. The as-prepared PLA blends showed elongation at break 40 times higher than that of neat PLA. Annealed PLA/EGMA blends had impact strengths over 50 times higher than that of the neat PLA. These improvements in mechanical properties were achieved without sacrificing the heat resistance of PLA. It was deduced that crystallization of the PLA matrix plays a significant role in toughening.

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